Title of the Synopsis :

ANALYTICAL STUDIES ON SOME CARCINOGENIC PESTICIDE IN VARIOUS ENVIRONMENTAL SAMPLES OF CHHATTISGARH

INTRODUCTION :

Agriculture in developing countries has become strongly dependent on the use of chemical substances in order to control insects and other plagues, aiming to enhance productivity. However environmental and human health problems caused by the extensive use of these chemicals mainly of pesticides have been reported worldwide [(1)]. There are over 1100 pesticides from a broad range of classes that are widely used in various combinations at different stages of cultivation or during post harvest storage to protect crops against pests and fungi and to provide quality preservation[(2)]. Pesticides and related compounds are very hazardous and lethal for organism as well as for humans. Long term exposure of pesticides and related compounds are cause long term health problems such as respiratory, memory disorders, dermatological conditions, cancer, depression, neurological deficiencies, miscarriages and birth defects have been known to be associated with pesticide exposure [(3)]. People are continuously exposed exogenously to varying amounts of pesticides that have carcinogenic or mutagenic properties. Heterocyclic amines represent an important class of carcinogens in food [(4)]. Various groups of pesticides are cause different types of health effects. Data shown in Table (I)

Carcinogenic pesticides encompass the variety of chemicals to kill or repel unwanted organisms such as insects, animals, weeds and micro-organisms from infesting lawns, gardens and crops[(5)]. Carcinogenic pesticides are a group of environmental pollutants that pose a significant risk to human health. Due to their constant use and chemical stability, these toxic pollutants are widespread and may persist as contaminants in the ambient environment [(6)]. The carcinogenic pesticides are highly publicized class of environmental pollutants. Unlike other pollutants whose domain are restricted, pesticides spread to every part of the environment; soil, sediments, rivers, lakes, ponds, groundwater, ocean and even air. Certain pesticides have the ability to persist for a long time in the environment [(7)].

Carcinogenesis is a multistage process by which various normal cells are transformed into cancer cell. Carcinogenesis can be initiated by chemical agent's example: tobacco, smoke, certain metals, pesticides, physical agents like ionizing radiation ultraviolet radiation, minerals, fibers such as asbestos etc. [(8)]. Carcinogenesis begins when carcinogens (cancer causing substances) damage the DNA in a cell or cause changes in other cell components or cell activities that can predispose them to cancer. The International Agency for Research on Cancer (IARC) considers that the compounds are associated with cancer in humans like Arsenic, Asbestos, Benzene, Mustard gas, soot, tar and mineral oil vinyl chloride CCl_4, and various pesticide groups[(9)].

The worldwide utilization of carcinogenic pesticides is about two million tons per year. Many older no patented, more toxic, environmentally persistent and low cost chemicals are used widely in developing nations, creating severe sensitive health problems and local and global environmental impacts. Pesticides introduction has also been associated with high cancer risks and reproductive problems in agricultural workers. In general, it has been observed that organophosphates are responsible for deaths in more than 70% of pesticide death cases [(10)].

CONSUMPTION OF CARCINOGENIC PESTICIDE IN INDIA

In India, agriculture is the backbone of the economy. Nearly 65% of the workforce derives livelihood from agriculture and are therefore exposed to chemical pesticides. India is the fourth largest pesticide producer in the world after the U.S., Japan and China. Domestic consumption is around 39 thousand metric tones (TMT). The production of Indian pesticide industry has almost remained stable at 82000-85000 metric tons (M.T.) during financial year 2010 [(11)].

CONSUMPTION OF CARCINOGENIC PESTICIDE IN CHHATTISGARH: -

Chhattisgarh is predominantly a tribal state, where about 85% of the people depend upon agriculture with rice as the main crop. Agriculture and related activities release vast amount of pesticide and other toxicants. The annual consumption of pesticides in Chhattisgarh state for year 2003-04, year 2004-05, year 2005-06, year 2006-07, year 2007-08, year 2008-09, year 2009-10, year 2010-11, and 2011-12 are 377.36 metric tons (M.T.), 415.88 M.T., 449.30 M.T., 487.05 M.T., 400.00 M.T. 410.00 M.T., 570.00 M.T. and 600.00 M.T. respectively and demand 2012-13is 800 M.T. [(12)].

Major objectives to be achieved :

- Development of new sensitive, selective, cheaper and refine spectrophotometric method for the detection and determination of various carcinogenic pesticides and related compounds in various environmental samples of Chhattisgarh.
- Sample is to be prepared by extraction of pesticide using an efficient and selective solvent followed by clean-up procedures to remove interfering species.
- Determination of the level of pesticide residue qualitatively and quantitatively with their breakdown products in the cleanup extracts using simple sensitive and selective spectrophotometric method will be done as an alternative of costly sophisticated instrumental techniques.

A Brief Review of the work already done

Various methods are used and many techniques have been developed for analyzing detection and determination of pesticides include Liquid Chromatography-Mass Spectrometry(LC/MS)[13], Gas Chromatography with Electron-Capture Detection[14], Gas Chromatography-Mass Spectrometry Determination[15], Reversed-Phase Liquid Chromatography-Gas Chromatography using the Through-Oven Transfer Adsorption/Desorption Interface[16], Two-Dimensional Capillary Gas Chromatography-Time-of-Flight Mass Spectrometry[17], Microwave Accelerated Selective Soxhlet Extraction with Gas Chromatography/Mass-Spectrometry[18], Biosensor Detection[19], Microwave Assisted Extraction and GC-FPD Analysis[20], Liquid Chromatography/Electro spray Ionization tandem Mass-Spectrometry(LC/ESI-MS) and Ultra High Performance Liquid Chromatography Quadrupole Time-of-Flight Mass-Spectrometry(UHPLC QqTOF MS) [21], Gas Chromatography-Ion Trap Mass-Spectrometry[22], Cloud Point Extraction and High-Performance Liquid Chromatography[23] etc. Most of the above mention instrumental methods and techniques are most expensive, quite elaborate, require expensive instruments, maintenance, too sophisticated for field measurement and are difficult to be used in the routine analysis of different matrices.

Noteworthy Contribution in the field of proposed work :

Earlier some work has been already done at school of Studies in Chemistry,Pt. Ravishankar Shukla University, Raipur, Chhattisgarh. Simple and sensitive spectrophotometric methods, Thin Layer Chromatography (TLC), Solid Sorbent System and low cost monitoring methods have been developed for the detection and determination of some toxic pesticides in the environment.

A sensitive spectrophotometric method for the determination of widely used herbicide paraquat has been developed. Paraquat is reduced with glucose in an alkaline medium and the blue coloured ion obtained has been measured at 600nm. Beer's low is obeyed in range of 0.1 to 1.2 ppm of paraquat. The molecular absorptivity is found to be 1.26×10^5 mol^{-1} cm^{-1}. The standard deviation and relative standard deviation are found to be ±0.007 and 2.0% respectively for 5 µg per 10 ml of paraquat analyzed over a period of 7 days. The method is free from the interference of other commonly used pesticides and water ions. The application of the method, for the analysis of paraquat in plants, fruits, grains, water, blood and which has been reported [24].

A sensitive method has been developed for spectrophotometric determination of an organophosphorus pesticide dichlorvas by sodium hydroxide to give dichloroacetaldehyde which on coupling with phloroglucial give orange colour in alkaline medium. The dye shows absorption maxima at 475 nm and obeys Beer's low in the range of 10-100 µg/25 ml (0.4 - 4ppm) of solution. The Molar Absorbitivity and Sandell's sensitivity were found to be 4.53×10^4 l mol^{-1} $cm^{-1}$and 0.0048 µg cm^{-2} respectively. The method has been successfully applied for the determination of dichlorvos in water, agricultural soil and vegetables [25].

In this chapter a sensitive spectrophotometric method is proposed for the determination of widely used pesticide endosulfan. The method is based on the liberation of sulphur dioxide from endosulfan by adding acid reagent and alcoholic potassium hydroxide. The liberated sulphur dioxide is then passed through iodated solution and the iodine liberated is then reacted with N-chlorosuccinimide and leuco crystal violet. The absorbance of the crystal violet dye formed is measured at 592nm. Beer's low is obeyed in the range of 0.1-1.2 µg/25 ml (0.004-0.048 ppm) of the solution. The Molar Absorptivity were found to be 8.08×10^5 l mol^{-1} cm^{-1} and 0.005 µg cm^{-2} respectively. The method has been applied for the determination of endosulfan in water, soil and vegetables [26].

A new sensitive spectrophotometric method is developed for the determination of carbofurane, a widely used carbamate pesticide, at sub ppm level. The method is based on the hydrolysis of carbofurane under alkaline condition to carbofurane phenol (2, 3- dihydro 7-hydroxy-2, 2-dimethyl benzo furan) and then the subsequent coupling of the phenol with p-anisidine and N-chlorosuccinamide in the presence of a catalyst (i.e. a mixture of sodium nitroprusside and manganese dioxide). The greenish-blue dye formed obeyed Beer's low in the range 0.1-1.0 ppm of carbofurane. It has molar absorptivity 1.9×10^5 (±100) l mol^{-1} cm^{-1} and has the maximum absorbance at 660 nm. The method is simple, sensitive and free from the interference of other common pesticides and ions. The method has been successfully applied to the determination of carbofurane in polluted water, soil, foliages and biological samples. It is also compared with other recently reported spectrophotometric methods [27].

A sensitive and selective spectrophotometric method for the determination and residue of carbaryl in field water grapes, vegetables and blood sample in described. The method is based on the diazotization of p-amino benzoic acid with sodium nitrite/hydrochloric acid and its coupling with 1-naphthol obtained from hydrolysis of carbaryl in alkaline medium. Beer's low in obeyed in the range of 0.1 ppm to 0.8 ppm. The pink coloured dye obtained shows absorbance maxima at 520nm. The dye could be extracted in isoamyl alcohol and has stability of 24 hour [29].

A new spectrophotometric method for the determination of dinocap in water and spray residue is described. The method is based on the reduction of 2, 4,-dinitro-6-actyl phenyl crotonate to 2, 4-diamino-6-octyl phenyl crotonate by Zn/HCl, the diamino compound. So formed is later diazotized and subsequently coupled with NEDA to form an azo dye having absorbance maximum at 545nm. The Beer's low obeyed in the range of 4.8 to 33.6 ppm. The important analytical parameter and optimum reaction condition are evaluated [30].

Proposed Methodology :

- Survey of extensive used carcinogenic pesticides in working environment of Chhattisgarh.
- Literature survey is done to find out the analytical method developed and identifying the drawbacks existing in the reported methods.
- Sampling of various toxic pesticides from different selected areas of Chhattisgarh will be done.
- Collected samples will be then treated in laboratory as required.
- Development of new sensitive, selective, cheaper and refine spectrophotometric method for the determination of various carcinogenic pesticides and related compounds in various environmental samples.
- Simple Spectrophotometric analytical method will be developed to find out the pesticide concentration level in various environmental samples.
- Detection and determination of various classes of toxic pesticides such as: Organophosphate, Organoclorine, Carbamates, Pyrethroids, Methyl Bipyridyl, Triazine, Triazole etc will be done.
- Optimization of analytical parameters like pH, reagent concentration, temperature and diverse ion effects etc.
- Study of statistical parameters *viz*. standard deviation, relative standard deviation, correlation coefficient, molar absorptivity, sandell's sensitivity etc.

Expected Outcomes of the Proposed Work :

- The expected method will be simple and more sensitive than other spectrophotometric method reported for the determination of toxic pesticides.
- The expected method will be successfully applied for the determination of toxic pesticides in water, soil, food and biological sample.
- The practical scientific advantage of the proposed research work is to introduce awareness to the common people as well as other agencies to understand the health effect to the contamination of toxic pesticide in water, soil, and biological system.
- The expected method will be compared with other spectrophotometric method which will be rapid cheaper and good alternative of other costly and mostly sophisticated instrumental methods and low cost might be preferred in small laboratory.

TABLE: I

S.No.	Chemical Name	Classification	LD_{50} value mg/kg (rat) oral/dermal	Toxic Effects
1	Paraquat	Methyl Bipyridyl	20	Carcinogenic, Liver, Heart and Kidney Failure.
2	Bifenthrin	Pyrethroids	>2000mg/kg	Possible human carcinogenic, mutagen.
3	Acetamiprid	Phenyl Pyrazole	1064mg/kg	Carcinogenic, Dermal Toxic
4	Diazinon	Organophosphate	66-369	Causes headache, blurred vision, muscular vision and muscular weakness.
5	Hexaconazole	Triazole	1453mg/kg	Carcinogenic, Neurotoxic.
6	Atrazine	Triazine	1750-3090	Carcinogenic, Endocrine disruptor.
7	Tetraconazole	Azole	1248mg/kg	Carcinogenic, teratogen, mutagen
8	Propoxure	Carbamate	100	Carcinogen, mutagen, causes kidney and liver failure, coma leading to death
9	Cypermethrin	Pyrethroids	250	Carcinogenic, skin and eye irritation, effects the central nervous system, increases liver and kidney weights.
10	Deltamethrin	Pyrethroids	67	Carcinogenic, paralysis, dermatitis, edema.
11	Pentachloro phenol	Organochloro compound	27	Carcinogenic, eye and nose irritation, mutagenic and neurotoxic.
12	Dichloro Diphenyl Trichloro Ethane	Chlorinated Hydrocarbons	250	Causes headache, blurred vision, muscular vision and muscular weakness.
13	Cyprodinil	Organonitrogen	>2000	Inhibit action of cholinesterase, disrupt nervous system.
14	Difenacoum	Rodenticide	1.8-2	Nausea, Vomiting, anticoagulant poisoning.
15	Dimethoate	Organothiophosphate	60-387mg/kg	Carcinogenic respiratory paralysis, increased blood pressure.

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List of Published/Communicated/ Presented papers:

1) A paper entitled "Low cost Spectrophotometric determination of paraquat in Environmental and Biological Samples" has been presented in National Conference on Biological Science in Current Scenario at ST. Thomas College, Bhilai (C.G) India on 10th October 2012.

2) A paper entitled " A New reagent for the spectrophotometric determinnation of paraquat" has been presented in International Conference on Environment and Human Health organized by National Environmental Science Academy in association with Department of Botany, Jamia Hamdard at Indian National Science Academy, New Delhi, India on 28-29th November 2012.

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